Stabilizing Lithium-Metal Anode by Interfacial Layer

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SLAC National Accelerator Laboratory

Project ID: bat365

Overview

Timeline

- Start: Oct 1, 2016
- End: Sep 30, 2021
- Percent complete: 90%

Budget

- Total project funding $50,000k from DOE
- Funding for FY19 $10,000k
- Funding for FY20 $10,000k

Barriers

Barriers addressed

- Increasing the energy density of advanced lithium (Li) batteries beyond what can be achieved in today's Li-ion batteries is a grand scientific and technological challenge.

Partners

- Collaboration
  - Battery 500 PI's (Jun Liu, Jason Zhang, Jie Xiao, Wu Xu, Stan Williams, Ping Liu)
  - BMR program PI' s
  - Stanford: Prof. Jian Qin, Prof. Yi Cui

Project Objective and Relevance

- Develop lithium-metal based full batteries with 500 Wh/kg specific energy to power electric vehicle and decrease the high cost of batteries.

- Design and fabricate Li metal anodes with high capacity, high coulombic efficiency and long cycle life.

- Design and understand interfacial layers between lithium metal and electrolytes to overcome the intrinsic material challenges that lead to short battery life, including lithium metal dendrite formation and severe side chemical reactions during electrochemical cycling.

Milestones (Stanford/SLAC)

FY20

Q1, Quantifying inactive Li using B500 electrolytes and protocols (completed)
Q2, Develop new 3D anode structures and test such using coin cell standard protocols to achieve 300-350 Wh/kg (cell-level) for 200 cycles (completed)
Q3, Develop new polymer protective layers for Li anode, test and report such using coin cell standard protocols (completed)
Q4, Select 3D Li architectures and polymer protective layers for pouch cells (single layer and multilayers) (completed)

FY21

Q1 Compare new Li anode architecture with 50 micron Li anode using protocols for 350 Wh/kg cells (completed)
Q2, Measure solid or semisolid (oxides, polymer or composites) electrolyte performance using protocols for 350 Wh/kg cells (SLAC) (completed)
Q3, Characterizing Li metal-solid electrolyte interface with cryoEM (completed)
Q4, Develop a new polymer as interfacial layer or solid electrolyte (in progress)

BATTERY 500 CONSORTIUM

Approach/Strategy

Advanced design and understand of interfacial layers at Li metal-electrolyte interface

1)Understand various factors impacting Li metal deposition, including electrolyte solvents

2)Engineer various interfacial protection materials with excellent chemical and mechanical stability, both inorganic and polymeric, to suppress lithium dendrite formation during electrochemical cycling and to improve Coulombic efficiency.

Structure and property characterization

1) Ex-situ transmission electron microscopy & scanning electron microscopy
2) Cryo electron microscopy
3) X-ray photoelectron spectroscopy
4) Nuclear magnetic resonance (NMR) spectroscopy

Electrochemical testing

1) Coin cells and pouch cells
2) A set of electrochemical techniques (ultramicroelectrode, etc.)

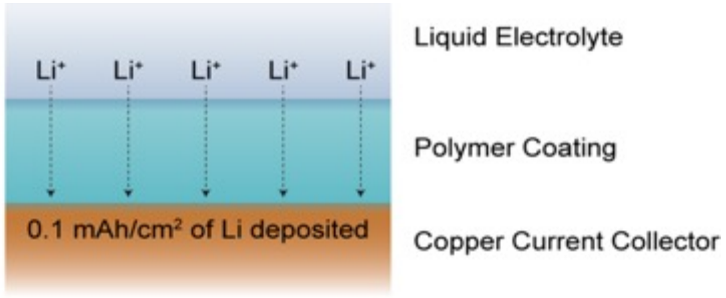
Theoretical modeling

1) Calculation of solvation structures

Technical Accomplishments and Progress

- Proposed a new design concept for polymer protective coating

- Mechanical instability of Li metal deposition is addressed by using a dynamic, viscoelastic polymer coating prevents pinholes, non-uniform Li deposition and accommodate volume expansion
- Chemical instability of Li metal deposition is addressed by tuning polymer coating solvation of Li ion and reduce electrolyte solvent swelling



Mechanical instability → Dynamic, viscoelastic

Chemical instability → Solvation | Swelling

} SEI | Ion transport | Li deposition

Z. Bao, Y. Cui et al. ACS Energy Lett. 1247–1255 (2016)

Y. Cui, Z. Bao et al. J. Am. Chem. Soc. 139, 4815 (2017)

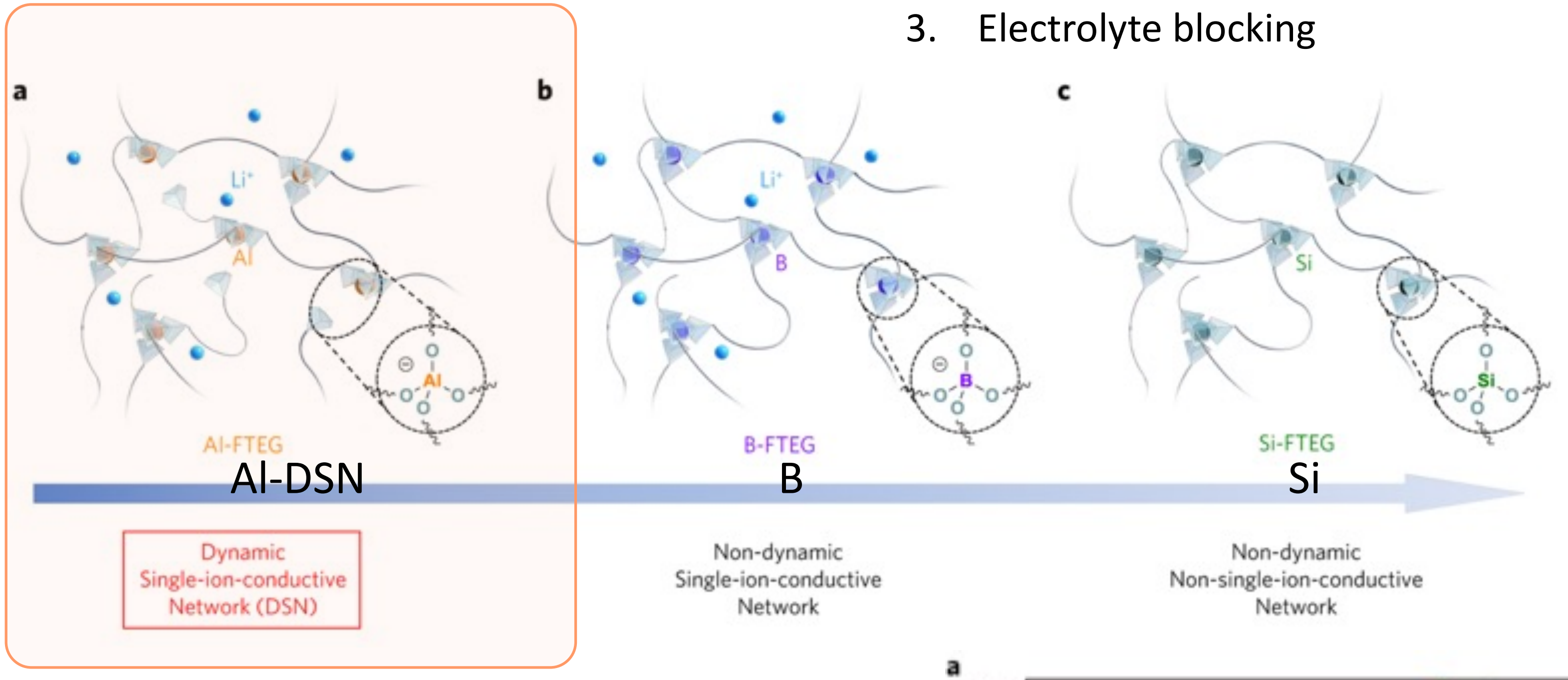
Z. Bao, Y. Cui et al. J. Am. Chem. Soc. 140, 11735–11744 (2018)

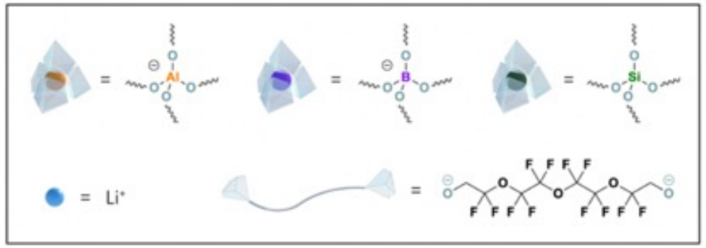
J. Qin, Z. Bao, Y. Cui et al. Adv. Funct. Mater. 1910138 (2020)

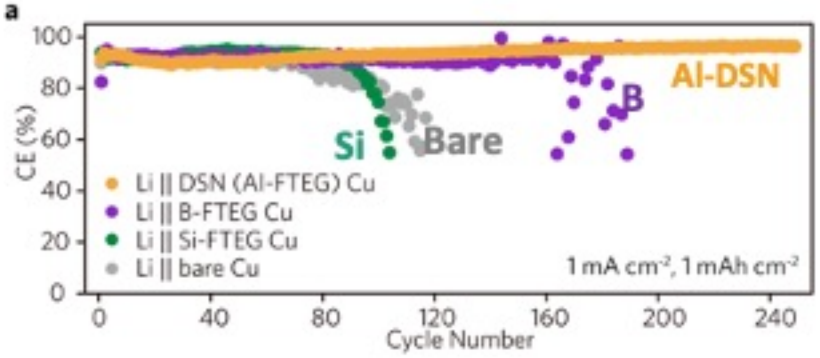
Technical Accomplishments and Progress

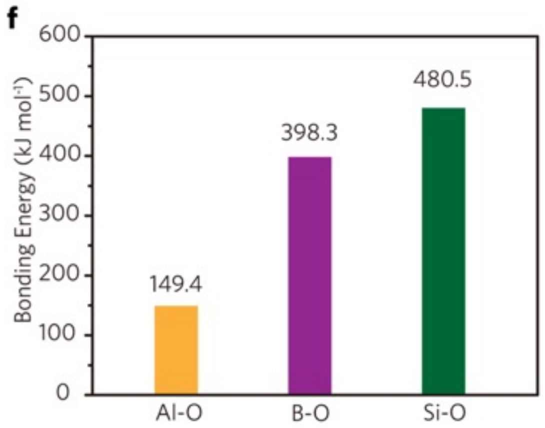
- Artificial SEI design with multifunction in a single matrix

1. Dynamic flowability
2. Fast Li^+ single-ion conduction
3. Electrolyte blocking









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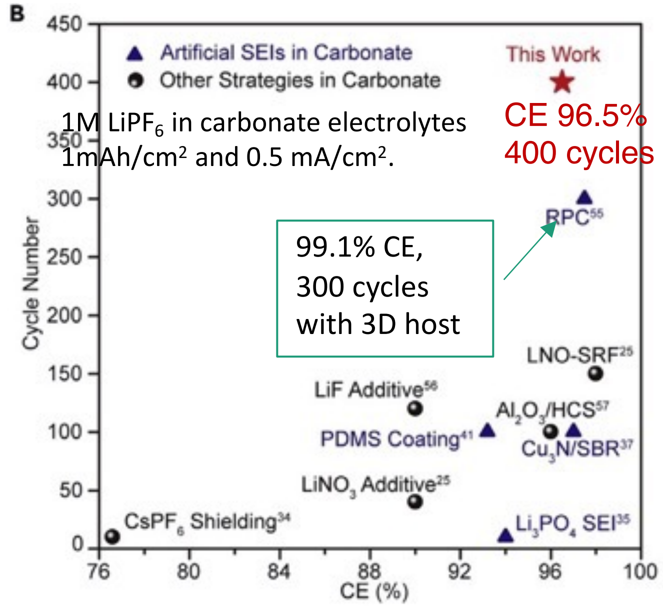
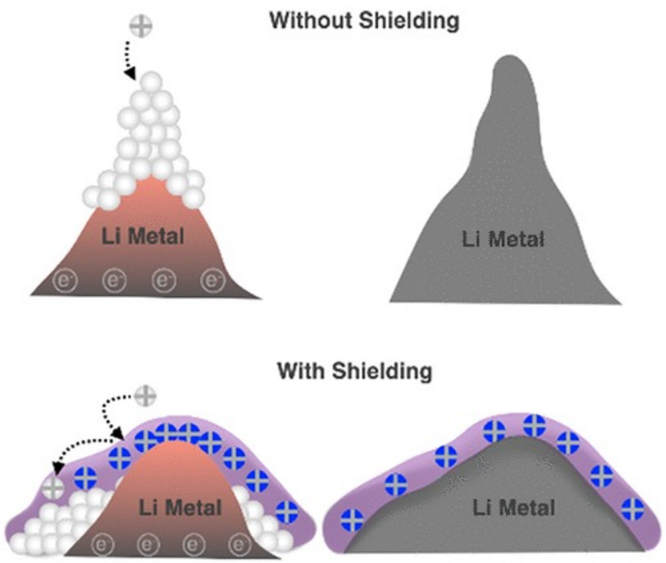
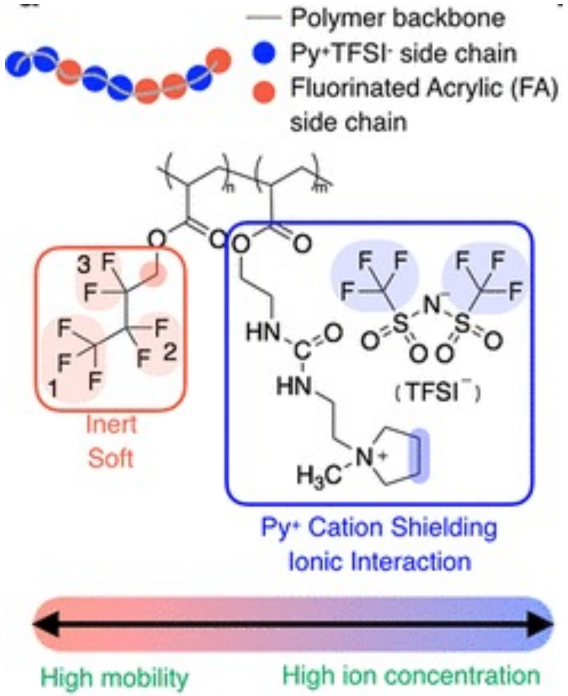


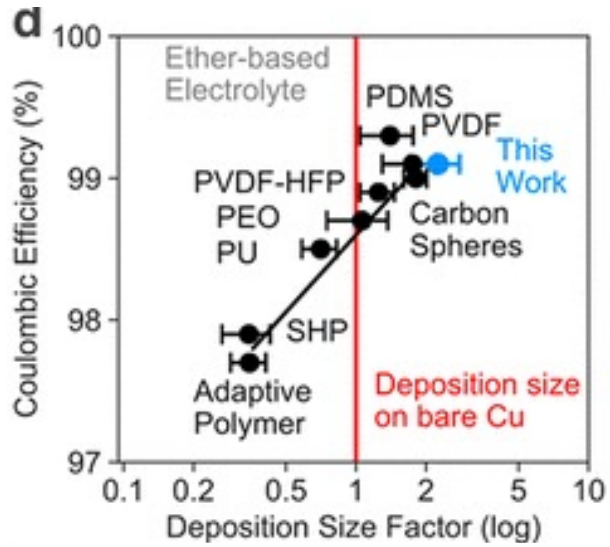
Z. Bao, Y. Cui et al. **Joule**, 3, 2761-2776, 2019

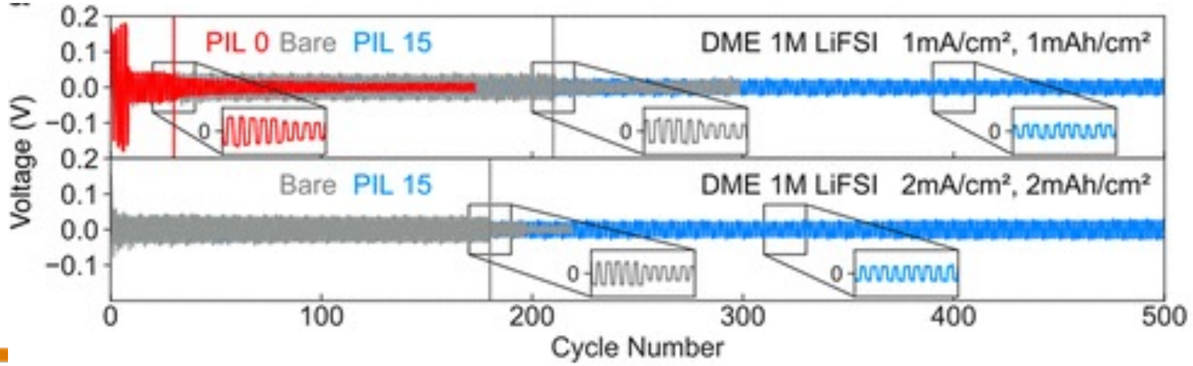
Technical Accomplishments and Progress

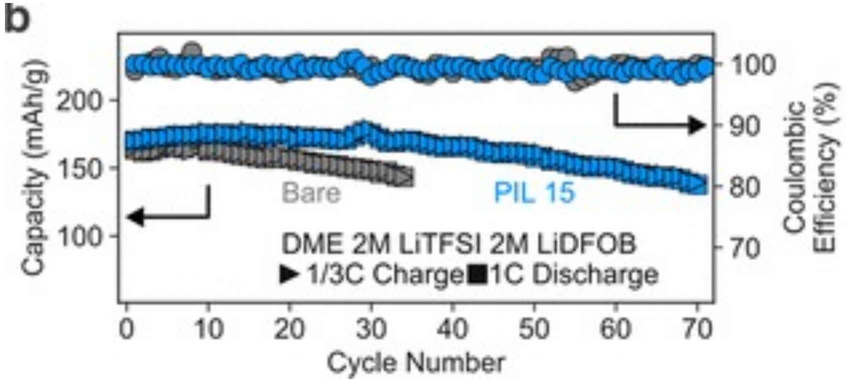
- Designed a cation-tethered flowable artificial SEI for Li metal











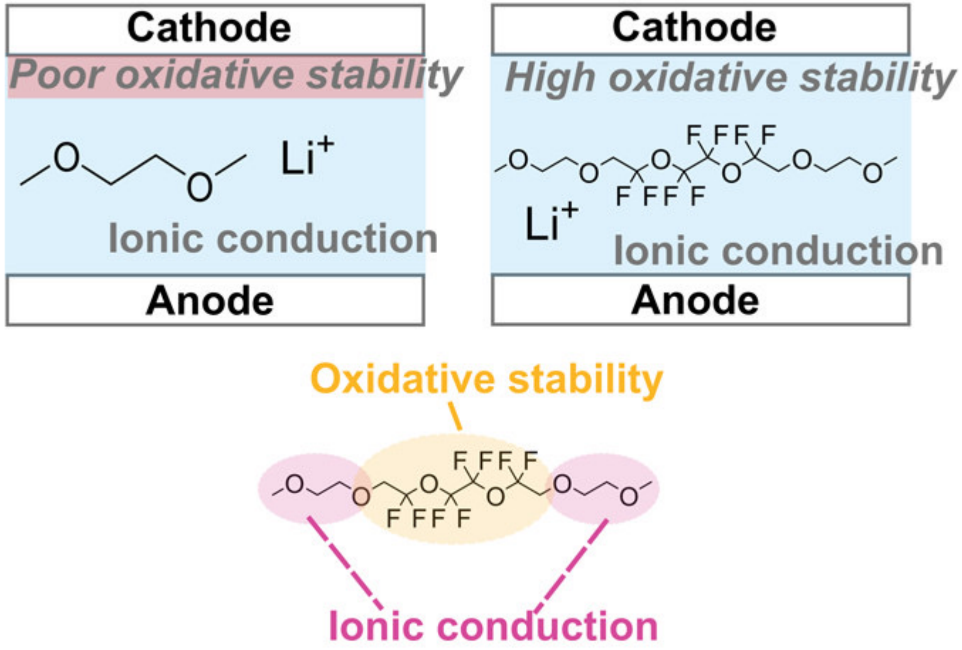
Z Huang+, S Choudhury+, H Gong, Y Cui, Z Bao, ***JACS***, 2020

Technical Accomplishments and Progress

In addition to the polymer coating, understanding electrolyte solvent design and its impact on Li metal deposition is necessary for proper interface layer design

First, we investigate solvent molecule design that will have required oxidative stability to pair with high-V NMC cathodes

- Increased oxidative stability with $-CF_2$



C. V. Amanchukwu, Z. Yu, X. Kong, J. Qin, Y. Cui, Z. Bao, **J. Amer. Chem. Soc.**, 142, 7393-7403, 2020.

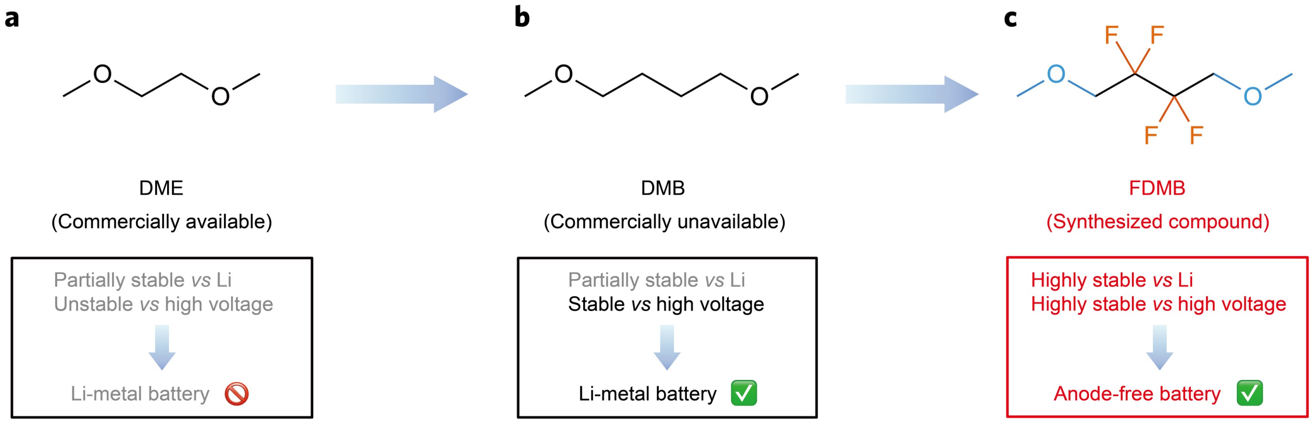
BATTERY500 CONSORTIUM

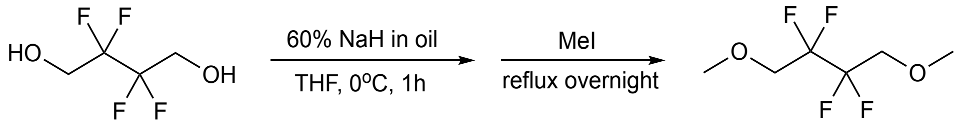
Technical Accomplishments and Progress

Understand various factors impacting Li metal deposition, including electrolyte solvents

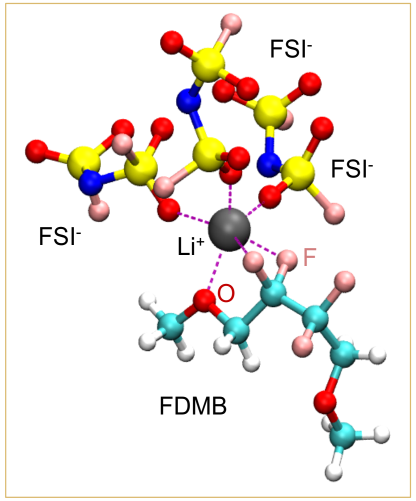
- Rational molecular design of electrolyte solvents

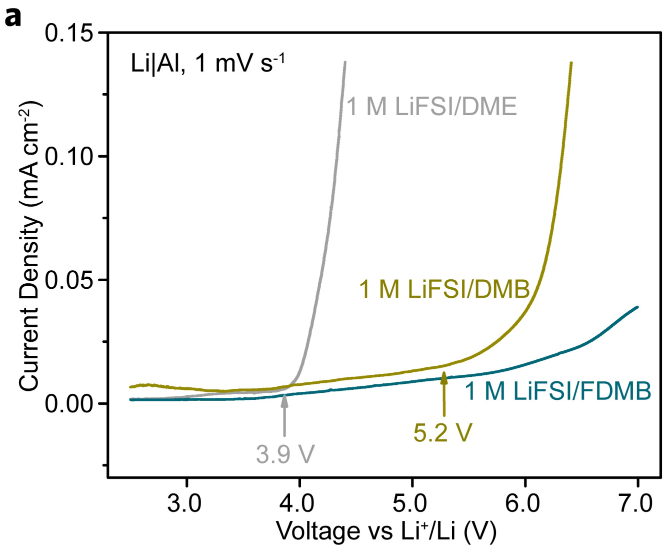
Anion derived SEI
High oxidative stability
Low salt concentration, large scale





Low-cost synthesis



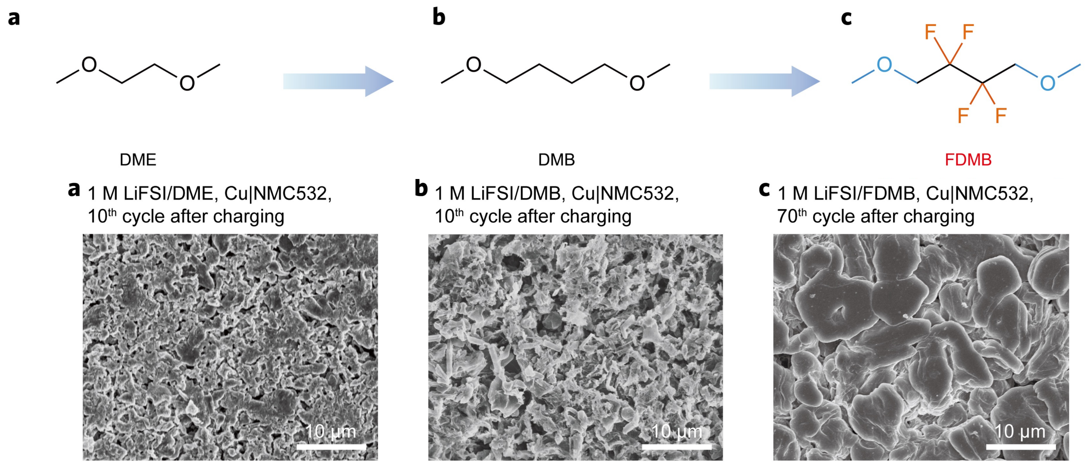


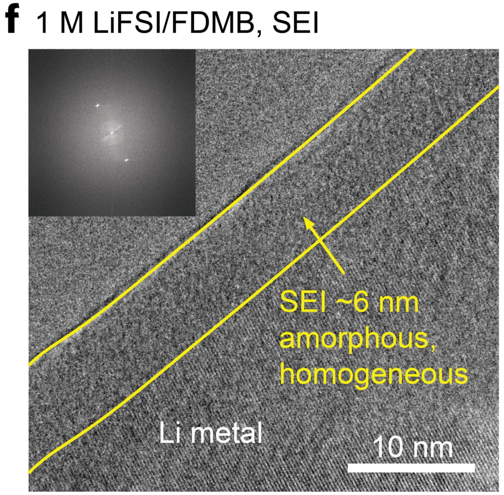
BATTERY CONSORTIUM 500

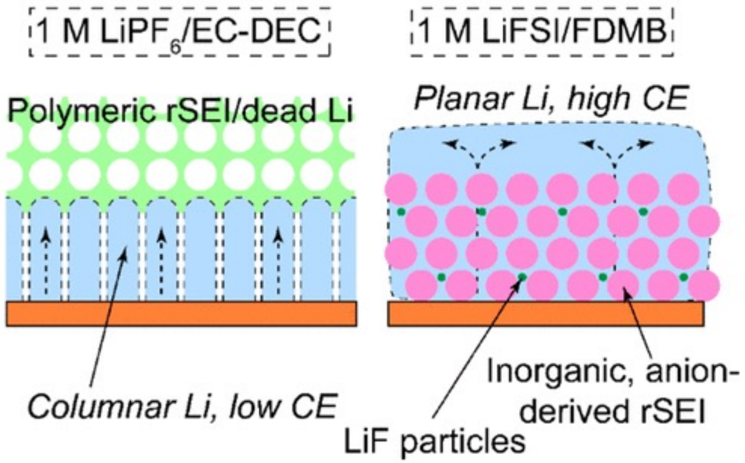
Z. Yu+, H. Wang+, Y. Cui, Z. Bao et al. ***Nature Energy*** 2020, *5*, 5264.

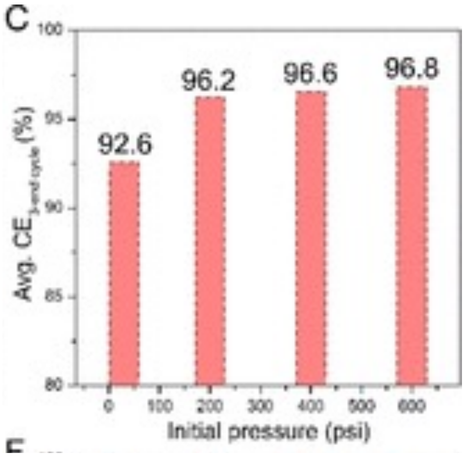
Technical Accomplishments and Progress

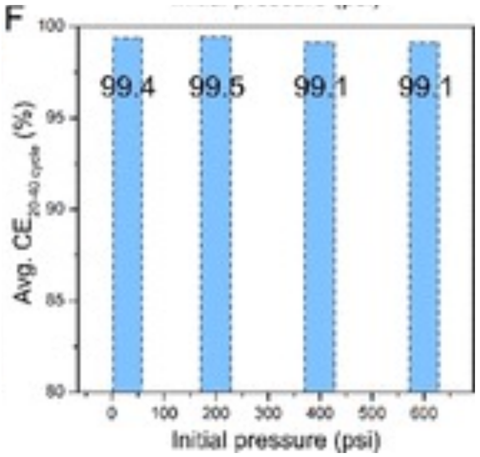
- New molecular design of electrolyte solvents- anion derived SEI











Z. Yu⁺, H. Wang⁺, Y. Cui, Z. Bao et al. ***Nature Energy*** 2020, *5*, 5264.

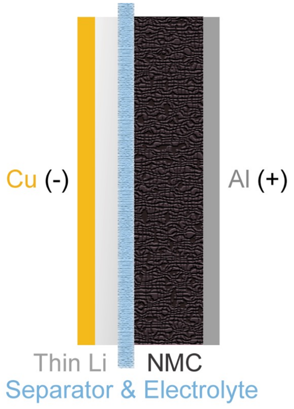
H. Wang, Wi. Huang, Z. Yu,.Z. Bao, Yi Cui, et al. ***ACS Energy Lett***. 2021, 6, 2, 816−825

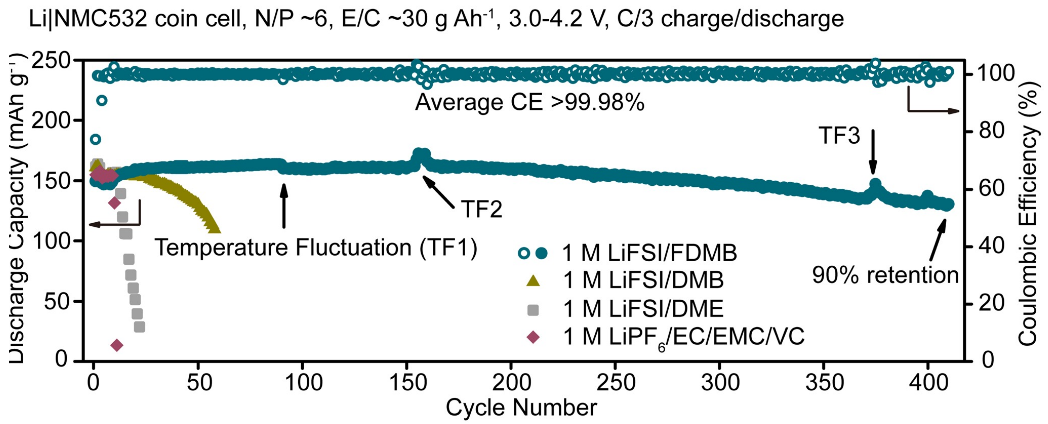
BATTERY500 CONSORTIUM

Technical Accomplishments and Progress

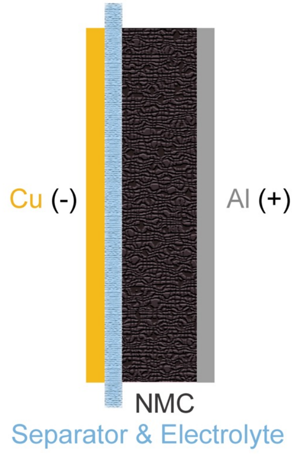
- New molecular design of electrolyte solvents- anion derived SEI
- Enable stable full-cell operation, even anode-free pouch cell

Li/NMC532 full cell

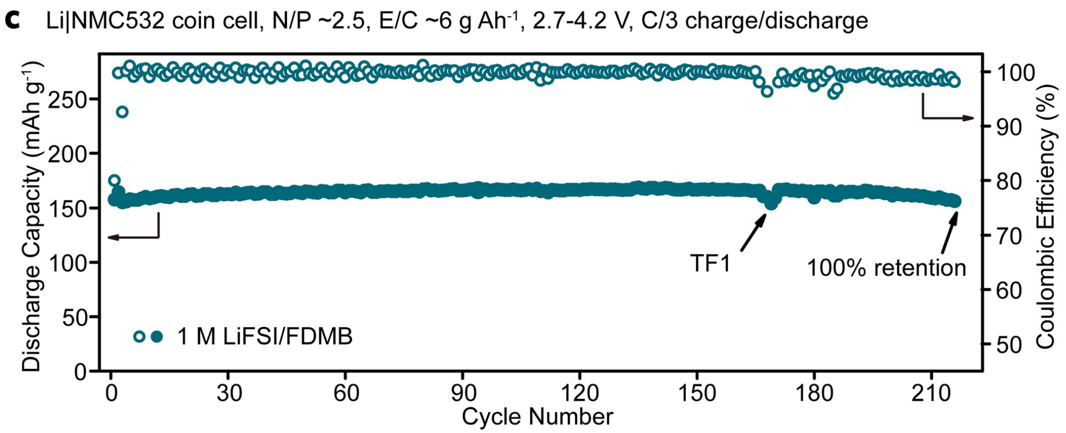


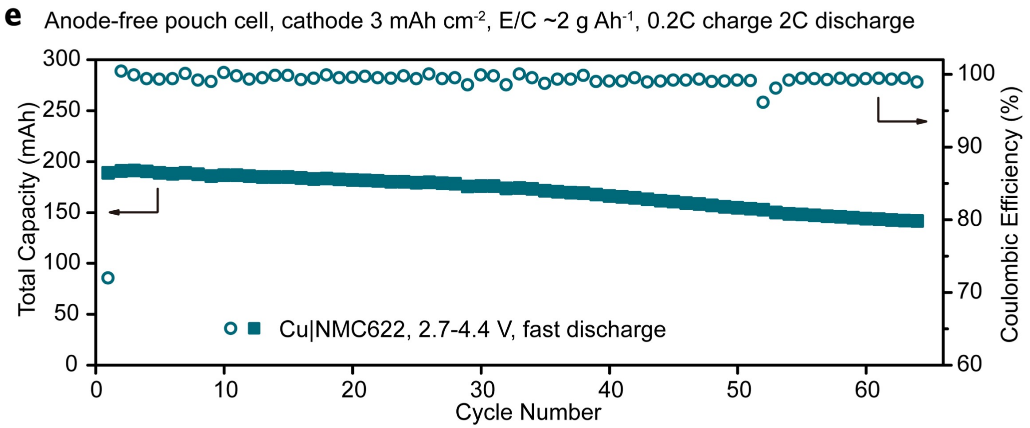


(2) Anode-free battery



Anode-free Cu/NMC622 pouch cell





Z. Yu⁺, H. Wang⁺, Y. Cui, Z. Bao et al. ***Nature Energy*** 2020, *5*, 5264.

Summary

- **Objective and Relevance:** The goal of this project is to develop stable and high-capacity Li metal anodes and the full battery cells to enable high energy lithium metal-based batteries to power electric vehicles, highly relevant to the VT Program goal.

- **Approach/Strategy:** This project combines advanced molecular design, organic synthesis, characterization, battery assembly and testing, and guided by simulation and cryogenic electron microscopy study.

- **Technical Accomplishments and Progress:** This project has produced important artificial SEI design rules, meeting milestones. They include identifying the key issues in lithium metal batteries, using rational materials design, synthesis, characterization and simulation. The results have been published in top peer-reviewed scientific journals. The PI and students involved have been recognized by various awards.

- **Collaborations and Coordination:** The PI has established a number of highly effective collaborations.

- **Proposed Future Work:** Rational future plan has been proposed.

Responses to Previous Year Reviewers' Comments

- Milestones also included investigation of 3-D host framework for the Li anode, but this was reported in a different presentation (BAT361). A number of the slides were identical for the two presentations, which confuses the assessment.
Response: The milestones listed were for the entire SLAC team as it was how we submitted our plans.

- Data of the kind presented on Slide 7 should be presented with error bars.
Response: this is noted for future review.

- Progress was clear, but the reviewer was unsure how the modeling will impact further development of the polymer.
Response: modeling has been helpful in understanding solvation structure as well as predicting polymer properties.

- The reviewer also suggested that the teams focus on one problem at a time (Li-metal SEI) instead of both that SEI and a 3-D host for Li.
Response: Indeed, we have been focusing on one problem at a time. It was probably confusing as the overall approach and milestones were shown.

- Collaboration with other Battery500 investigators seems to be missing, as they are not co-authors on any cited works.
Response: we have sample exchanges with other Battery500 Pis. However, no joint publications yet.

- As noted above, the reviewer would possibly de-emphasize the 3-D host work here as other teams are pursuing that. Instead, focus on achieving a competitive CE and, somehow, convincing the team that a "soft" polymer will ever be able to stop dendrite formation and growth, or consider some other way to control dendrites.
Response: Again, we are sorry for the confusion about the 3D host approach which is not part of this PI work, but rather overall SLAC work. The pressure consideration only takes into account one aspect of Li metal deposition. Our work has already shown that with soft coating that is dynamic and solvent blocking, we can achieve very high CEs. Furthermore, our rationale molecular design of electrolyte solvent has been shown to be productive in realizing dense anion-derived SEI, beneficial for high CE.

Collaboration and Coordination

Battery 500 PI's:
Jun Liu
Jie Xiao
Jason Zhang
Wu Xu
Stan Williams
Ping Liu

SLAC/ Stanford University:
Prof. Yi Cui
Prof. Jian Qin

Remaining Challenges and Barriers

- It is challenging to generate Li metal with high coulombic efficiency and long cycle life to meet the Battery500 goal
- Coulombic efficiency is still not high enough to minimize lithium loss during extended cycles.
- Further designs to be tested to maintain a stable SEI when cycling lithium metal at high areal capacity.

Proposed Future Work

- To further develop artificial SEIs based on rational design rules assisted by simulation and cryoEM study.
- To combine promising artificial SEI with 3D Li host.
- To combine promising artificial SEI with high-performance electrolyte.

•Any proposed future work is subject to change based on funding levels